Low-cost, High Energy Si/Graphene Anodes for Li-ion Batteries

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Presenter: Rob Privette

Project ID: ES237

XG sciences
THE MATERIAL DIFFERENCE

XG Sciences, Inc.

June 6-10, 2016

Overview

Timeline

- Project start date: Nov. 15, 2012
- Project end date: Jul. 22, 2016
- Percent complete: 86%

Budget

- Total project funding
  - DOE share $1,147, 684
  - Contractor share $123,042
- Funding received in FY14
  - $499,990
- Funding for FY15
  - $499,909

Barriers

- Barriers addressed
  - Specific Energy
  - Life
  - Cost

Partners

- XG Sciences - Project lead
- A123 System
- Georgia Institute of Technology
- Collaborators
  - Argonne National Laboratory
  - Ashland Specialty Ingredients
  - Daikin America
  - JSR Micro
  - Lawrence Berkeley National Laboratory
  - Lubrizol
  - Sandia National Laboratory
  - Zeon Chemicals
  - Solvay

Relevance

Overall Objectives:

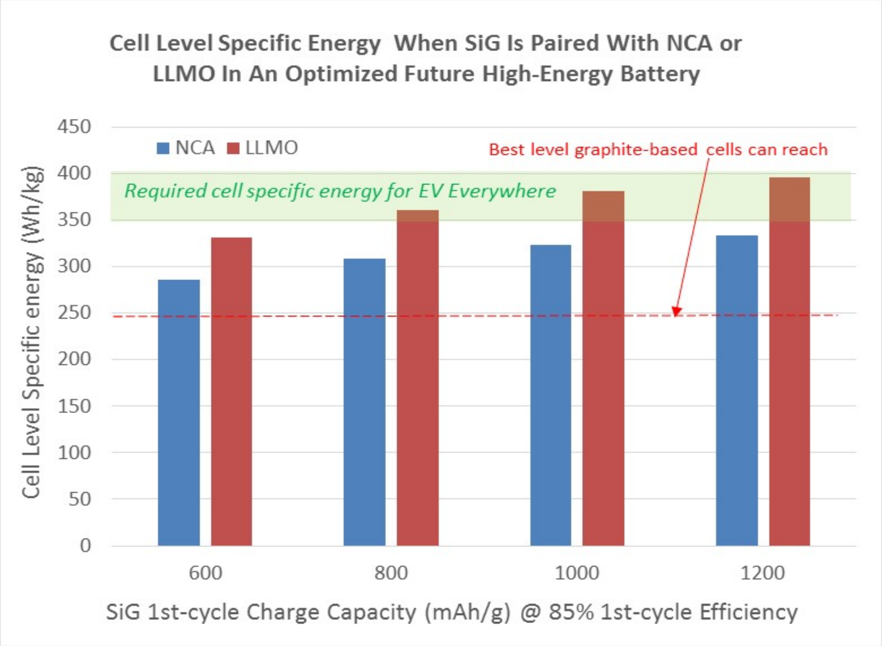
- Demonstrate XG SiG™ Si-graphene nano composite next generation Li-ion anode:
  - 600 mAh/g ***(Specific Energy Barrier)***,
  - 85% 1st cycle efficiency and
  - 1000 cycles with 75% capacity retention ***(Life Barrier)***
- Stabilize and optimize the XG SiG™ anode pilot production ***(Cost Barrier)***
- Develop a scalable dispersion and coating process with desired electrode properties
- Validate the XG SiG™ technology in commercial grade 2 Ah prototype Li-ion cells

Impact on Barriers

EV Everywhere program defines a cell specific energy target of greater than 350 Wh/kg with 1000 cycles

Project Objective #1: Improve XG SiG™ anode performance

a. 600 mAh/g (Energy Barrier),
b. 85% 1st cycle efficiency, and
c. 1000 cycles with 75% capacity retention (Life Barrier)



Impact on Barriers

EV Everywhere targets cutting battery costs to $125/kWh

- This has been one of the biggest challenges for Si-based anodes due to poor scalability and prohibitive process cost.
- XGS' XG SiG™ manufacturing process specifically addresses the cost issue in three ways:
  - Use of a low cost Si precursor,
  - Producing XG SiG™ in an existing manufacturing plant,
  - Automation and modular design of the production system making the XG SiG™ process less labor intensive
- Cost models show that XG SiG™ can achieve a competitive price as compared with graphite which is required for the commercial acceptance for PHEVs and EVs.

Milestones

Tasks	2014				2015				2016	
	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4	Q1	Q2
1. Improve EC performance of XG SiG™				MS1			MS2			
2. Optimize pilot production							MS3			
3. Characterize materials/electrodes/cells										
4. Optimize dispersion				MS4						
5. Optimize electrolyte/additives						MS5				
6. Design/build 2Ah prototype cells				MS6			MS7			

MS 1: Demonstrate XG SiG™ silicon anode material in full cells:
600mAh/g, 85% 1st cycle efficiency, 500 cycles with 70% retention
MS 2: Demonstrate 600mAh/g, 85% 1st cycle efficiency, 1000 cycles with 70% retention
MS 3: Demonstrate XG SiG™ manufacturing process readiness
MS 4: Demonstrate electrode coating ready for prototype cell builds 2~3 L slurry preparation
MS 5: Select final electrolyte / additive
MS 6 & 7: Demonstrate XG SiG™ performance in 2Ah cells

Status of Current Term Milestones

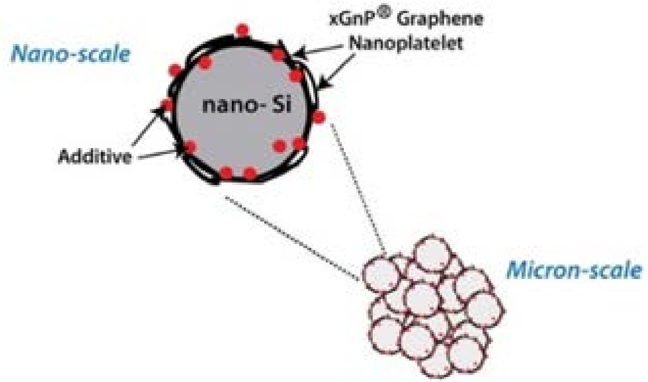
Milestone ID	Description	Status
2	**Demonstrate 600mAh/g, 85% FCE, 1000 cycles with 70% retention**	Cell demonstrated 600 mAh/g ; 88% FCE; 1000 cycles with ~85% capacity retention
3	**Demonstrate XG SiG™ manufacturing product and process variable limits**	Manufacturing product and process variable limits were defined and implemented resulting in improved and stable material quality
5	**Select final electrolyte / additive**	XGDA-3 electrolyte, xGnP Grade R-10 graphene nanoplatelet additive
7	**Demonstrate XG** SiG™ **performance in 2Ah cells**	2Ah cells demonstrated > 1000 cycles

Approach to Performance Improvement

Milestone: 600mAh/g, 85% FCE, 75% capacity @ 1000 cycles

Status: Demonstrated XG SiG™ material 600 mAh/g, >85% FCE and >75% capacity retention at 1000 cycles targets

- Employ material modification to target more stable SEI layer
  - Si precursor
  - Composite formulation
  - Composite manufacturing process



- Reduced Si fracture
- Reduced Li^+ reaction
- Optimized graphene nanoplatelet support

Approach to Manufacturing Process Improvement

Milestone: Demonstrate XG SiG™ manufacturing process readiness

Status: XG SiG™ manufacturing product and process variable limits were defined and implemented resulting in improved and stable material quality

- Define process capability
- Define XG SiG™ Product capability
  - Relate key performance to manufacturing metrics
- Demonstrate Manufacturing Process Control

Approach to Electrolyte and Additive Selection

Milestone: Selection of Electrolyte and Additives

Status: XGDA-3 electrolyte, xGnP Grade R-10 selected based on performance

- Identify:
  - Appropriate candidate electrolytes/ electrolyte additives,
  - Appropriate candidate conductive additives and loadings,
- Characterize applicable electrolytes and conductive additives
  - Single layer pouch cells and coin cells
- Select the best performing combination for 2Ah Cell Build

Approach to demonstrating SiG™ in 2Ah cells

Milestone: Demonstrate XG SiG™ performance in 2Ah cells

Status: 2Ah Cells meet program objectives ; 600 mAh/g ; 88% FCE (Half Cell); 1000 cycles with ~85% capacity retention

- Formulate optimized SiG™, electrolyte, binder, conductive additive, etc.
- Coat and characterize coatings at A123 Systems
- Build and characterize 2Ah Cells

Technical Progress

XG SiG™ met MS 2 target in 63 mAh pouch cells

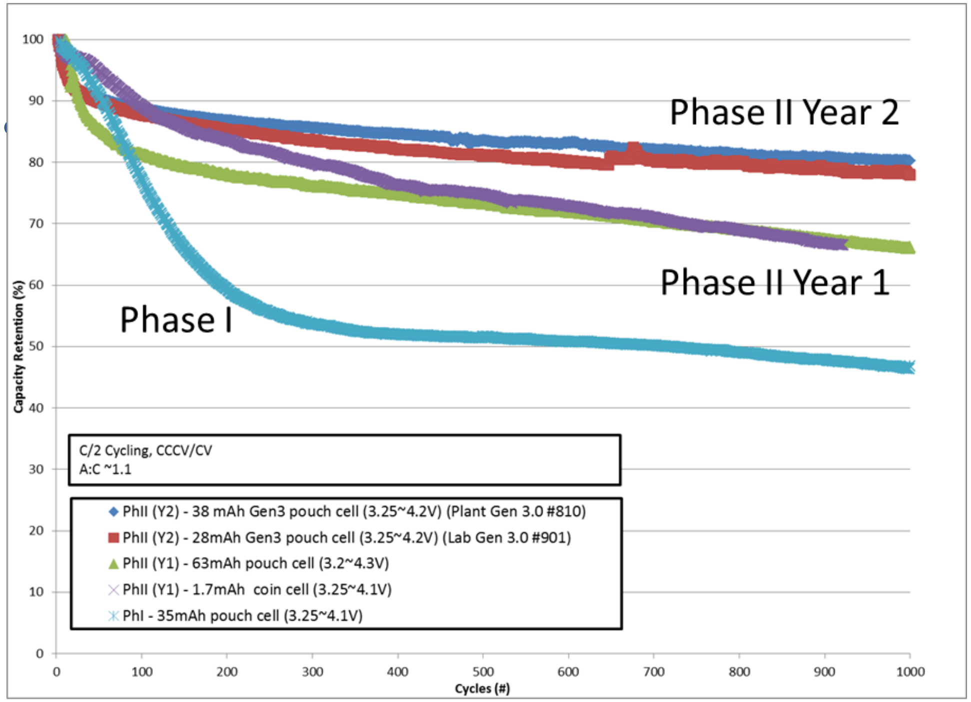
Demonstrated XG SiG™ material 600 mAh/g, 85% FCE and 70% capacity retention at 1000 cycles targets in small format cells

Improvement tied to: (a) modified Si precursor, (b) optimized formulation, and (c) manufacturing process modifications

❑ Anode
- 90% Active + 6% PAA binder + 4% conductive additive
- Active : lab and plant XGS Gen 3 (600 mAh/g, > 88% FCE)
- Conductive additive : lab and plant xGnP-10
- Loading : 2.5 mAh/cm² and 3.8 mAh/cm²
- Anode density: 1.55 g/cc for full coin cell

❑ NCA cathode
- 2.27 mAh/cm² for 2.5 mAh/cm² Gen 3 anode
- 3.45 mAh/cm² for 3.8 mAh/cm² Gen 3 anode

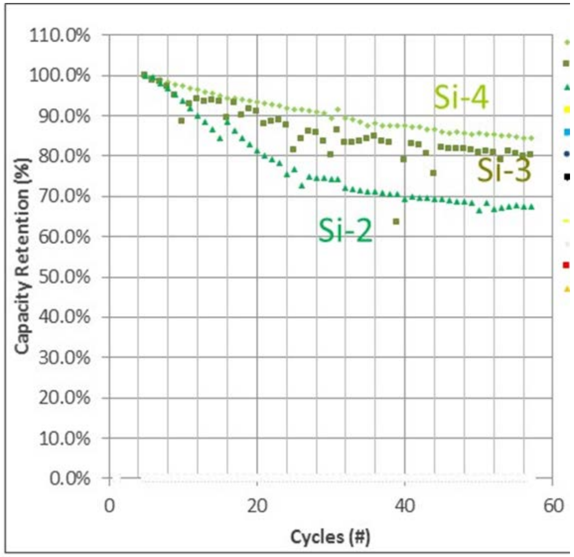
❑ Full cell & Test condition
- Gen3 SiG anode : NCA cathode = ~1.1
- Test protocol: 1C Cycling, Voltage as indicated

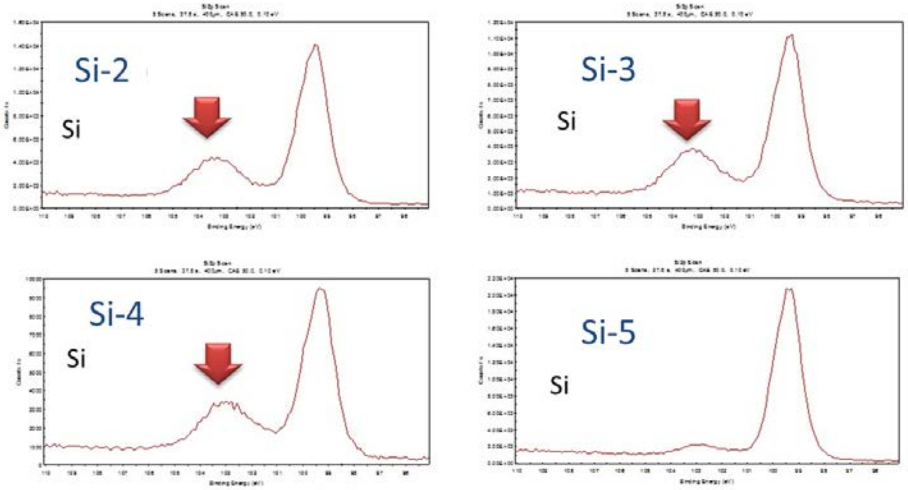


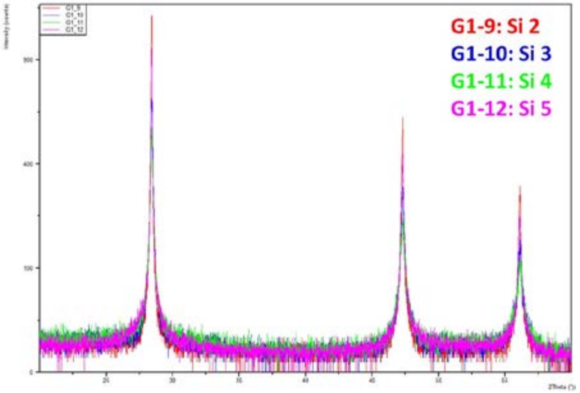
Technical Progress

Evaluation of New Si – Precursors

- Alternative Commercial Si Precursors Obtained
  - -Si-2 is standard Si-precursor for reported work
- Improved Cycling Performance (Half Cell)
  - - Si-3 and Si4 show inherent improved performance to Si-2
  - - Anode Capacity of 850 mAh/g
- Crystal Size
  - -The Si raw materials have different peak curve areas, indicating different particle or crystallite sizes
- Surface oxidation
  - - Si – 5 provides an opportunity to evaluate impact of oxygen content on XGS SiG Materials

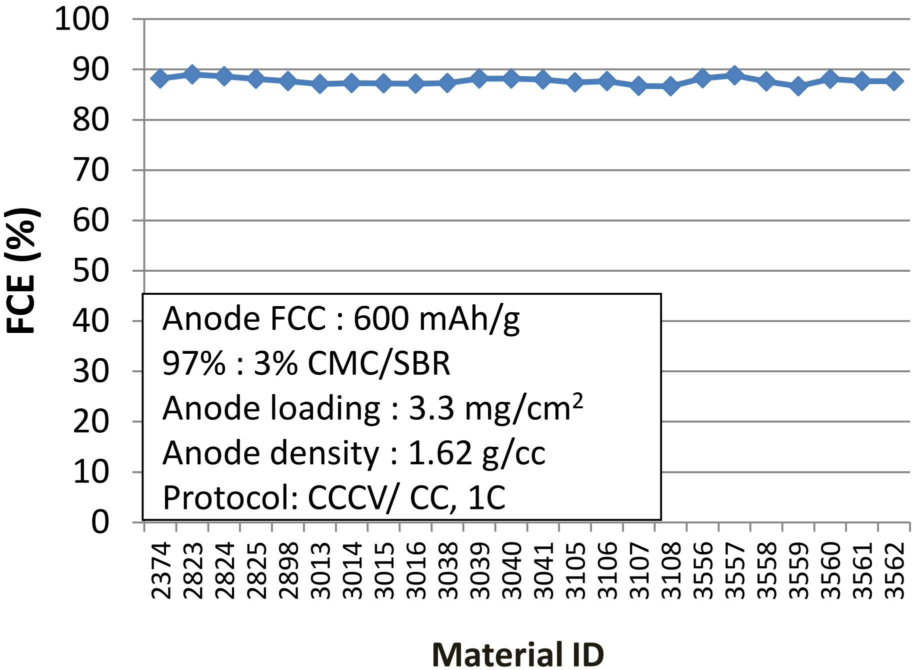


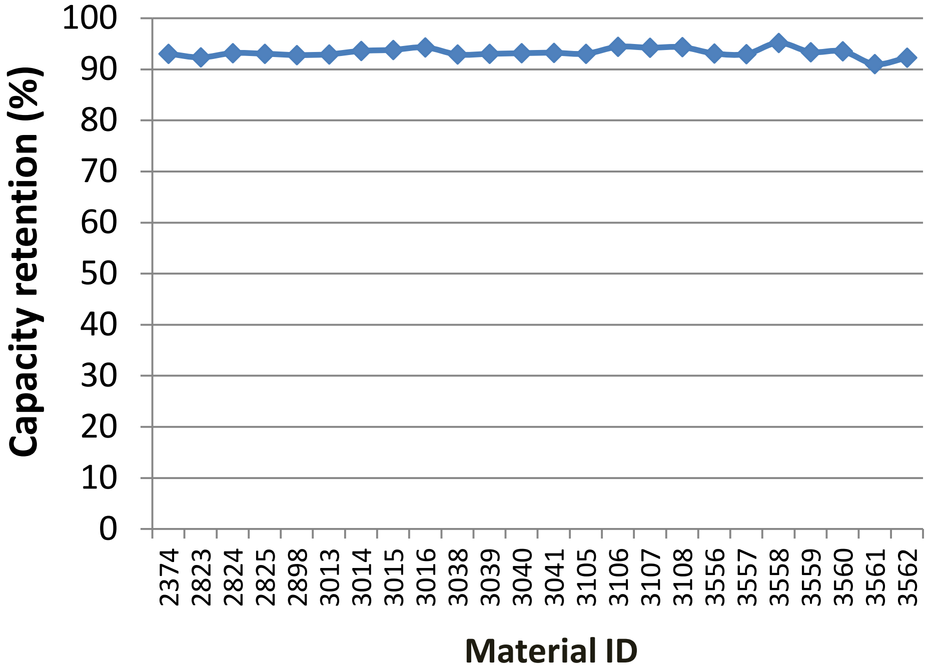




Technical Progress

Production material shows good consistency in 1st Cycle Efficiency and capacity retention in support of MS 3 - Manufacturing process readiness

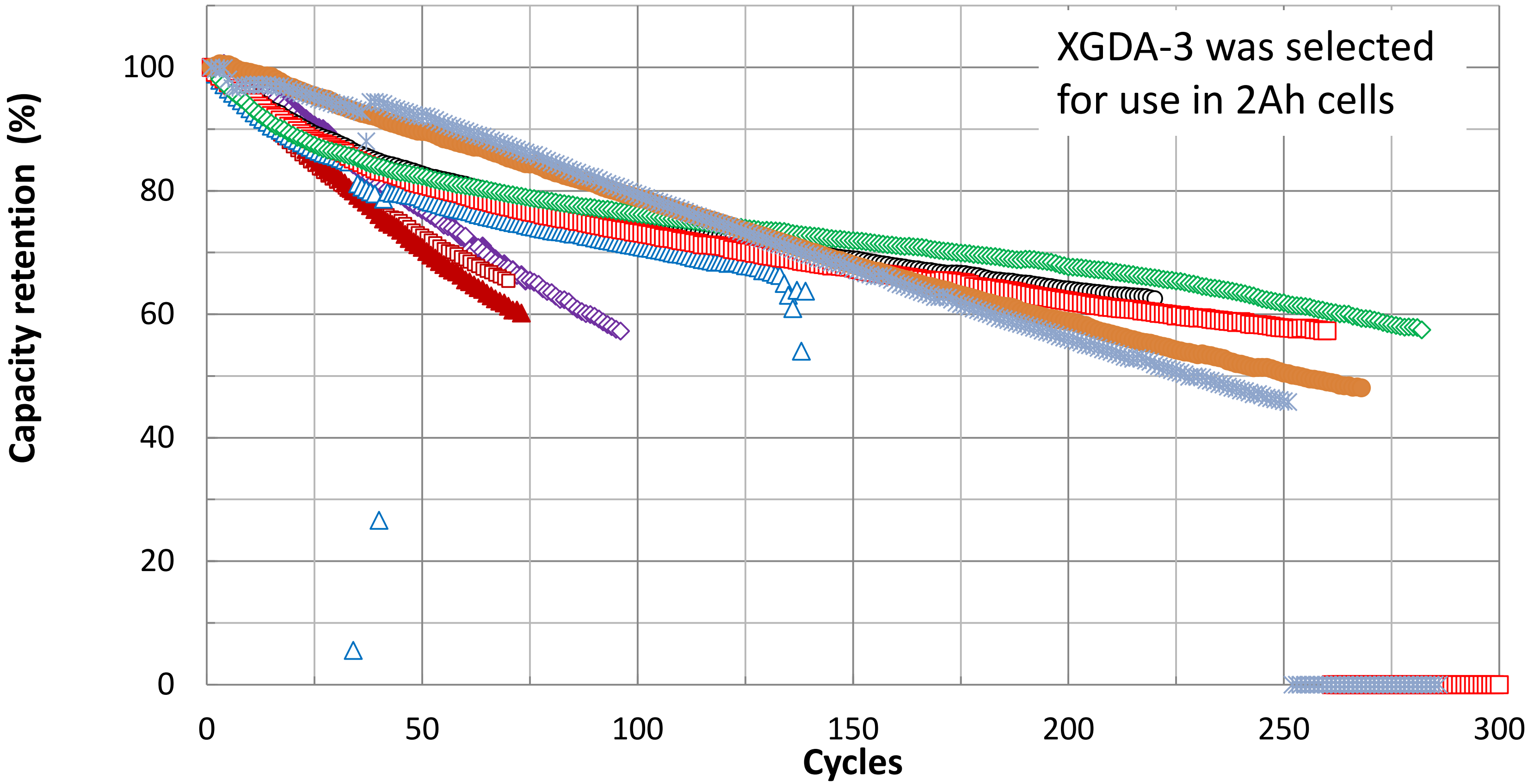




Technical Progress

Electrolyte / electrolyte additive selection was performed in combination with several partners.

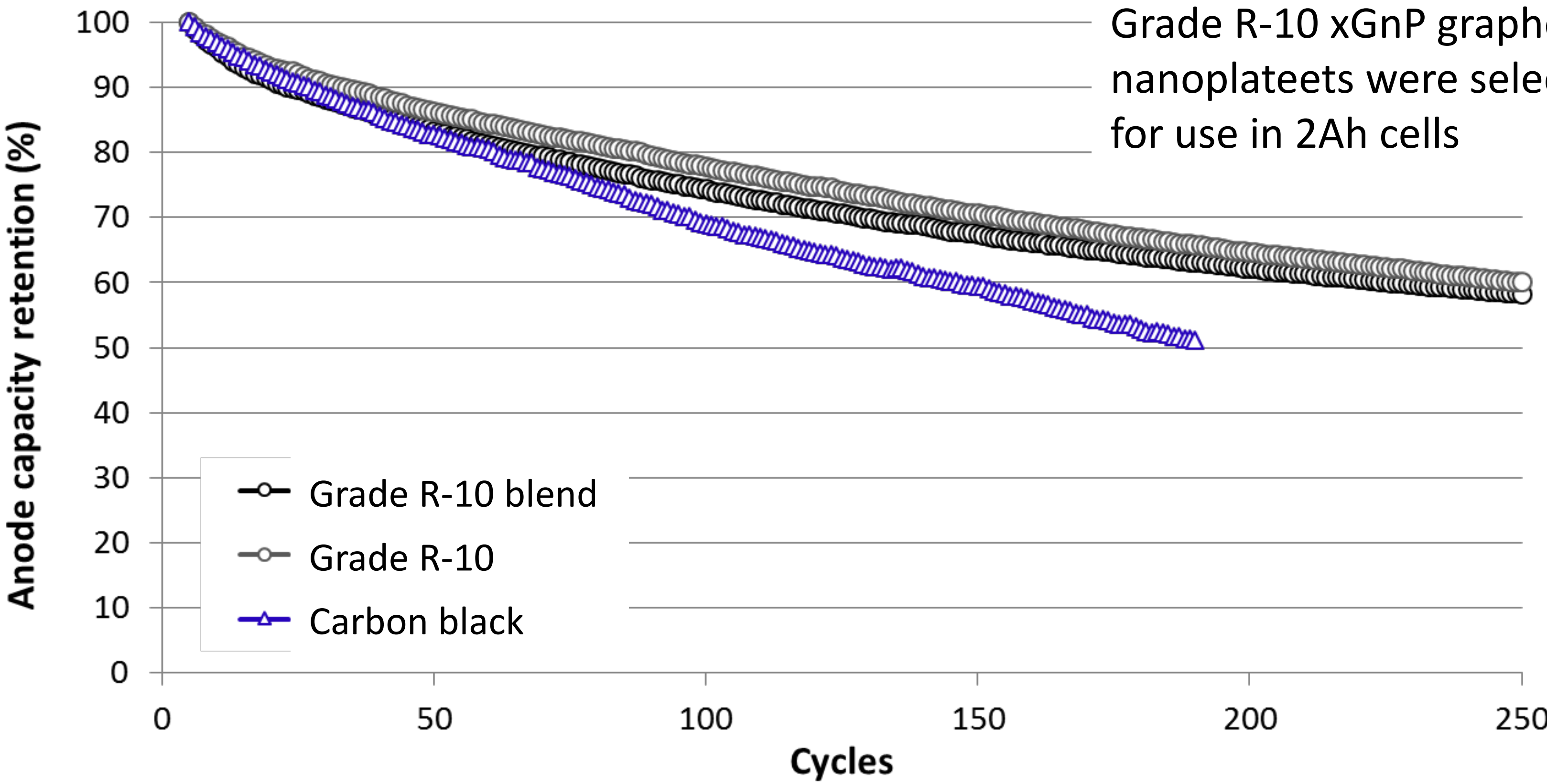
Coin cell testing considered: FCE, Capacity retention



Technical Progress

Anode conductive additive selection was performed in combination with several sources.

Coin cell testing considered: FCE, Capacity retention



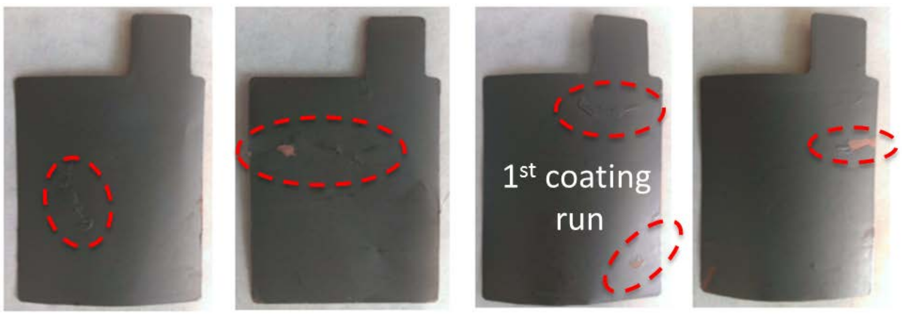
Grade R-10 xGnP graphene nanoplateets were selected for use in 2Ah cells

Technical Progress

2Ah Cell Build – Coating Optimization

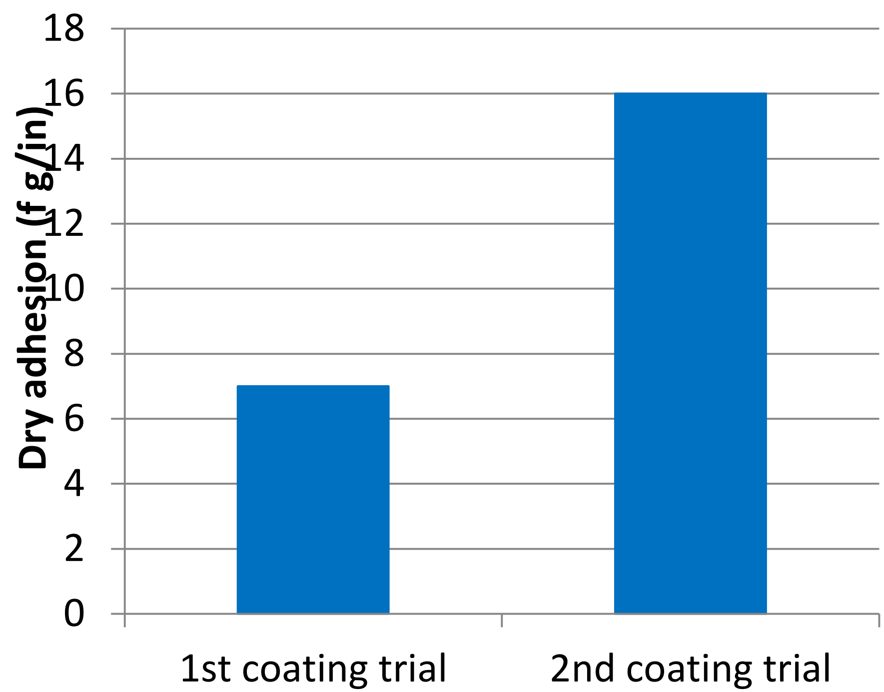
Optimized dispersion and drying conditions

SiG coating quality improved for 2Ah cell build



Modified dispersion protocol and drying condition => No streaks or flaking

- Dry adhesion improved by 2X over the first coating trial.
- Electrode passed all QC checks.



Technical Progress

2Ah Cell Build – Cell Design

- ❑ Anode
  - Slurry : 90% Gen3 SiG + 4% R10 conductive additive + 6% PAA
  - Loading : 5.68 mg/cm^2 per side
  - Electrode density : 1.55 g/cc
  - Thickness : 83um total

- ❑ NCA cathode
  - Loading : 27.7 mg/cm^2 double side

- ❑ Cell capacity
  - 2.11 Ah (without aging)
  - 1.83 Ah (with aging)

- ❑ A / C = 1.1

Technical Progress

2Ah Cell Build – Cell Build

1st cycle: +C/40, -C/40, 4.2-3.0V, 100% DOD, RT
HT aging: +C/10 to 100% SOC, aging for 3 days, degas/seal
Qualification: -C/10; +C/10, -C/10, then +C/5, -C/5, DCR, ACR check at 50% SOC, RT

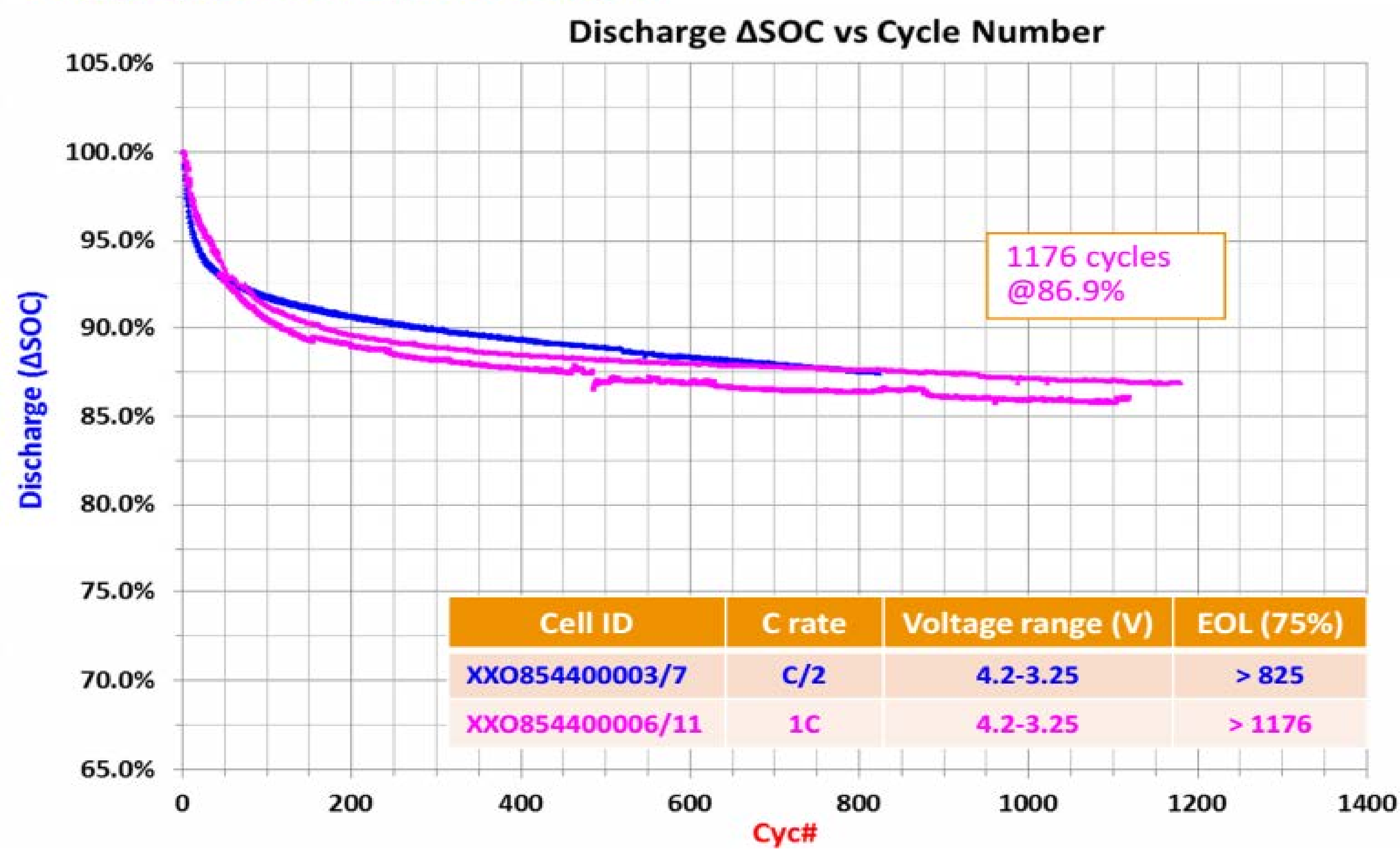
	Formation					Qualification (After 3day 45C)										
Cell ID	1st Chg (Ah)	1st Dis (Ah)	1C Chg (Ah)	ICL(%)	f-DCR (mΩ)	1st n-Dis (Ah)	2nd n-Dis (Ah)	% Ret	5A (Ah)	5A (Wh)	Avg V	DCR (mΩ)	n-ICL (%)	ACR (maccor)	Note
XXO854400003	2.962	2.453	2.471	20.75	0.00	2.326	2.348	99.06	2.311	8.359	3.617	26.09	26.150	11.080	XGS
XXO854400004	2.960	2.452	2.470	20.72	0.00	2.323	2.346	99.02	2.310	8.354	3.616	26.08	26.172	10.360	XGS
XXO854400005	2.975	2.464	2.484	20.74	0.00	2.336	2.359	99.03	2.320	8.394	3.618	26.30	26.113	10.890	XGS
XXO854400006	2.974	2.465	2.485	20.65	0.00	2.339	2.361	99.07	2.324	8.410	3.619	25.69	25.964	11.040	XGS
XXO854400007	2.994	2.484	2.502	20.53	0.00	2.355	2.377	99.07	2.338	8.464	3.620	25.43	25.957	10.660	XGS
XXO854400008	2.957	2.447	2.467	20.84	0.00	2.319	2.340	99.10	2.304	8.334	3.617	26.01	26.368	10.710	XGS
XXO854400009	2.984	2.472	2.490	20.71	0.00	2.344	2.366	99.07	2.328	8.420	3.617	26.09	26.120	10.520	XGS
XXO854400010	2.970	2.459	2.482	20.78	0.00	2.335	2.359	98.98	2.322	8.404	3.619	25.72	25.901	10.540	XGS
XXO854400011	2.977	2.470	2.489	20.53	0.00	2.344	2.367	99.03	2.330	8.433	3.619	25.36	25.771	10.660	XGS
XXO854400012	2.983	2.471	2.490	20.72	0.00	2.339	2.362	99.03	2.324	8.405	3.617	26.45	26.291	10.980	A123
XXO854400013	2.991	2.454	2.494	21.88	0.00	2.296	2.367	97.00	2.329	8.429	3.619	25.18	26.362	10.690	A123
XXO854400014	2.974	2.458	2.479	20.99	0.00	2.329	2.352	99.02	2.316	8.378	3.617	25.98	26.446	10.510	A123
XXO854400015	2.981	2.472	2.488	20.59	0.00	2.344	2.366	99.07	2.328	8.422	3.618	25.58	25.993	10.790	A123
XXO854400017	2.979	2.470	2.491	20.61	0.00	2.345	2.368	99.03	2.329	8.428	3.619	25.21	25.802	10.390	XGS
Average				**20.79**			**2.360**					**25.798**	**26.101**	**10.701**	

- Stabilized cell capacity @C/10 (4.2~3.0V)
  - 2.36 Ah
  - 11.8% over design max. (**2.11 Ah**)

Technical Progress

2Ah Cell Build – Cycling

+C/2, -C/2, 4.2-3.25 V, 100% DOD, RT

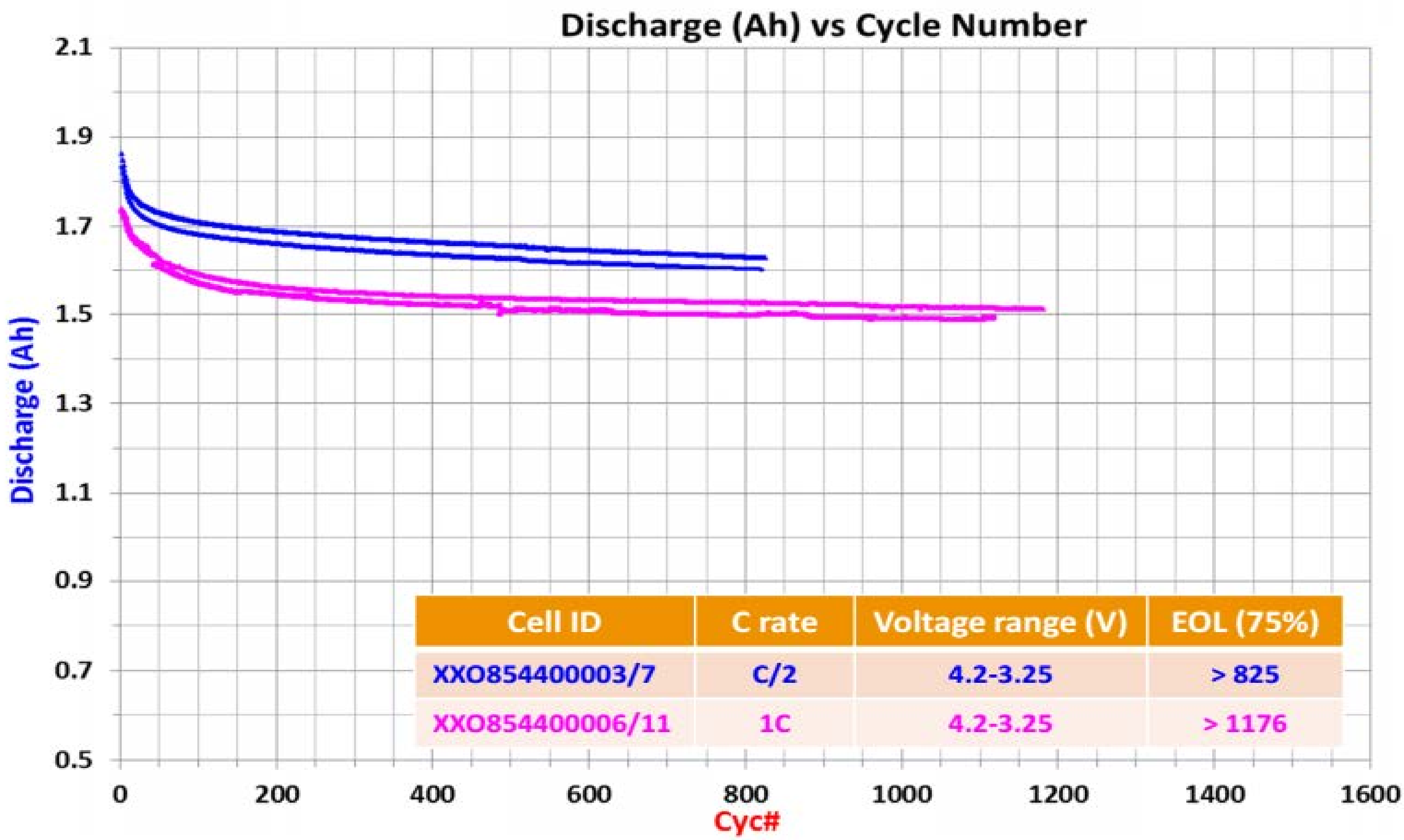


Cell ID	C rate	Voltage range (V)	EOL (75%)
XXO854400003/7	C/2	4.2-3.25	> 825
XXO854400006/11	1C	4.2-3.25	> 1176

Technical Progress

2Ah Cell Build – Cycling

+C/2, -C/2, 4.2-3.25 V, 100% DOD, RT



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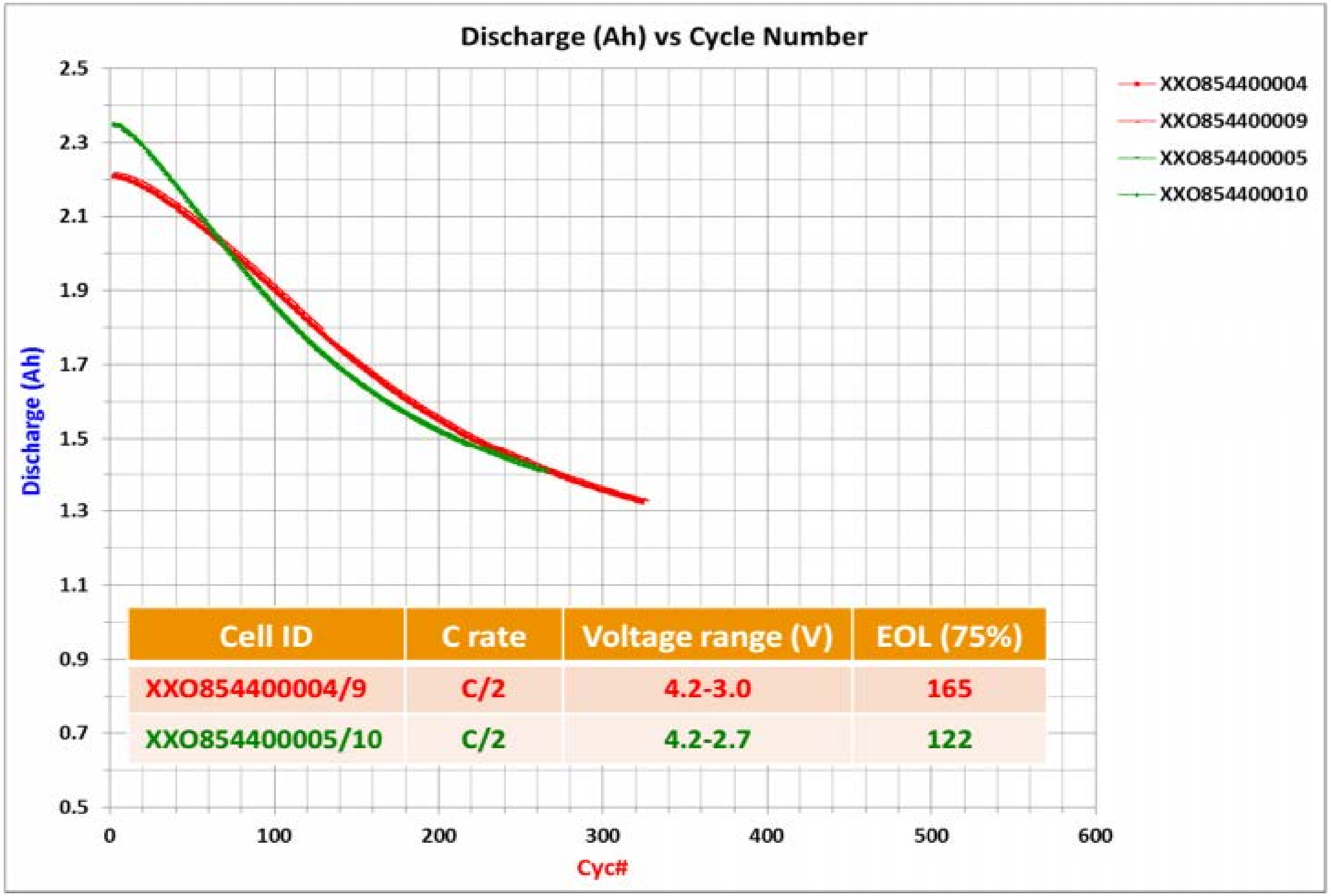
XXO854400003/7	C/2	4.2-3.25	> 825
XXO854400006/11	1C	4.2-3.25	> 1176

Technical Progress

2Ah Cell Build – Cycling

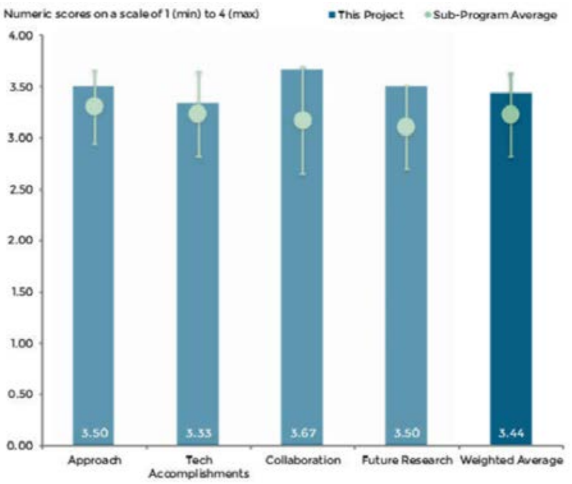
+C/2, -C/2, 4.2-(2.7~3.25) V, 100% DOD, RT



Cell ID	C rate	Voltage range (V)	EOL (75%)
XXO854400004/9	C/2	4.2-3.0	165
XXO854400005/10	C/2	4.2-2.7	122

Responses to Previous Year Reviewers' Comments

2015 Reviewer Comments	Response
The path to both scale-up and cycle life is not clear.	XG Sciences currently operates a ~50 Ton/year plant for XG SiG™. Scale-up to 250 Ton/year plant is planned but outside the scope of this project. Cycle life has been improved but additional work is still necessary. Pathway to improved cycle life focuses on enhancing Si/graphene interface to provide additional protection from electrolyte reactions.
There are still significant technical barriers to overcome in this project	Agreed. Additional technical developments are needed in order for high capacity silicon anodes to be able to meet automotive requirements. While this project has made progress, more work is needed especially in capacity retention and swelling.
Need to see more information on volumetric energy density and rate capabilities of this material	The cells used in this program are not optimized for volumetric or gravimetric energy density. Thus reporting this information would not accurately represent commercial capabilities or performance. XG SiG 2Ah cell capacity retention as a function of C-rate is shown here.



Rate	% retention
C/10	100.0
C/5	98.5
C/2	93.8
1C	90.9
2C	84.8
5C	30.8

Collaboration & Remaining Challenges

- Collaborations and Coordination
  - XG Sciences – Prime
  - A123 Systems – Subcontractor
  - Georgia Institute of Technology – Subcontractor
  - Argonne National Laboratory (A. Jansen)
  - Ashland Specialty Chemicals
  - Daikin America
  - Lawrence Berkeley National Laboratory (G. Liu)
  - Sandia National Laboratory (C. Orendorff)
  - JSR Micro
  - Lubrizol
  - Zeon
  - Solvay

- Remaining Challenges
  - Further improve capacity retention performance over larger voltage window
  - Improve initial (1^{st} 100 cycles) capacity retention performance

Proposed Future Work

Barrier	Proposed work	Objective (MS)

Specific Energy,
 	
Life
	• Optimize SiG Formulation utilizing newly identified potential Si-Precursors
	    • Improved cycle life observed in half cells
	    • Reduce overall electrode expansion through tailored crystal size
		Demonstrate:
		600 mAh/g,
		85% FCE,
		85% Cap retention @1000 cycles
		<50% expansion

Specific Energy,
 	
Life
	• Improve SiG graphene conductive coating
	    - Optimization of graphene XGS coating process to improve coverage and SEI formation protection
	        - Small Business Voucher Program Underway w/ LBNL
	        - DE-FOA-0001417, SBIR/STTR FY 2016 Phase I proposal submitted
		Objective:
		Improved voltage window performance, 850 mAh/g,
		85% FCE,
		75% Cap retention @500 cycles

Summary

- XG Sciences has met program objectives
  - Goals met for Si anode performance based on 2Ah cycling.
  - Further improvements in voltage window are desirable
- All material developments
  - Transferred to high capacity plant production, material at numerous cell customers.
- Slurry and coating developments
  - Transferred to A123 Systems and numerous other cell manufacturers.

2015 Program Objectives	2015 Program Accomplishments
Demonstrate 600mAh/g, 85% FCE, 1000 cycles with 70% retention	Cell demonstrated 600 mAh/g ; 88% FCE; 1000 cycles with ~85% capacity retention
Demonstrate XG SiG™ manufacturing product and process variable limits	Manufacturing product and process variable limits were defined and implemented resulting in improved and stable material quality
Select final electrolyte / additive	XGDA-3 electrolyte, xGnP Grade R-10 graphene nanoplatelet additive
Demonstrate XG SiG™ **performance in 2Ah cells**	2Ah cells demonstrated > 1000 cycles